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THE TOXICOLOGY OF TITANIUM TETRACHLORIDE

I. V. Sanotskiy*

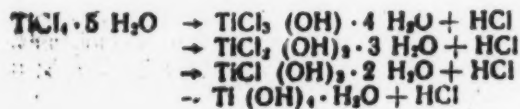
Metallic titanium in the form of wrought titanium has extremely valuable mechanical properties (high limit of stress, yield point, and proportionality). It has an extremely good strength to weight ratio. The strength of titanium is almost twice as high as that of pure iron, and nearly 6 times higher than that of pure aluminum. The mechanical strength of titanium at increased temperatures is significantly higher than that of other metals; at 425°, for example, it is almost twice as high as that of the strongest aluminum alloy at 200°. The indicated circumstances make titanium an extremely promising material in machine building.

From a hygienic standpoint, the most important product of producing metallic titanium is titanium tetrachloride, which also has independent significance as a polymerization catalyst. The goal of this report is to attract attention to certain characteristics of the toxic effect of TiCl_4 .

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TiCl_4 is an extremely mobile transparent liquid with a boiling point of $+136^\circ$. Vapor tension is 10 mm Hg at 20° , and 26 mm Hg at 40° . It has been shown that TiCl_4 itself does not dissociate.

TiCl_4 hydrolyzes extremely easily in the air. According to the data of T. P. Luchinskiy, hydrolysis occurs according to the following equations:



orthotitanic acid (colloid).

The kinetics of these reactions have not been established. It is assumed that the first two compounds (solids) are extremely unstable, while, at the same time, the penultimate one (a white solid) is relatively stable. It has been shown that the hydrolysis of TiCl_4 to TiO_2 never occurs under ordinary conditions.

Literature on the toxicity of titanium tetrachloride is extremely limited. F. I. Vanin attributes the vapor that forms during the hydrolysis of TiCl_4 to neutral vapor without toxic properties. Karotstsi felt that the toxicity of TiCl_4 is wholly determined by the HCl that forms from it. The data of Ye. A. Nel'nikova indicate that the toxicity of titanium tetrachloride is higher than that of hydrogen chloride, since it is assumed that the finely dispersed products of hydrolysis are capable of penetrating deep into the lungs up to the very alveoli, where hydrolysis continues and hydrogen chloride is liberated in statu nascendi, acting directly on the alveolar epithelium.

In our experiments in studying toxicity, we first detected a strong scatter of the lethal concentrations that could not be explained so long as air humidity was not considered. A simple device for conditioning the air was created (Figure 1). The investigations established that with an increase in atmospheric humidity, the toxicity of products of TiCl_4 hydrolysis decreased. Thus, for example,

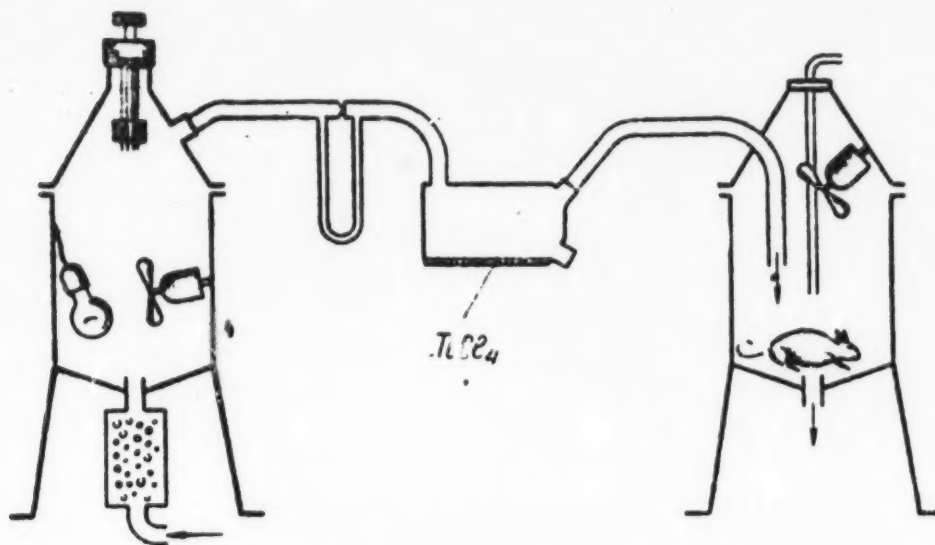


Figure 1. Diagram of the air conditioner

at an absolute humidity of 5.7 mm Hg, the products of TiCl_4 hydrolysis at a concentration equal to 0.78 mg/l with respect to titanium killed 100% of the animals, but at a humidity of 10.2 mm Hg, with approximately the same concentration of titanium ions, only 80% died. At a humidity of 7.41 mm Hg, 50% of the animal deaths occurred at a concentration of titanium ions of 0.16 mg/l; at a humidity of 14.38 mm Hg, the same mortality rate was caused by a concentration of titanium ions three times higher (0.52 mg/l).

The general mortality data are given in Figure 2. We used 150 albino mice and 50 albino rats.

It is apparent in Figure 2 that, with a relatively low humidity (5 - 7 mm Hg), the toxicity of products of hydrolysis, if one judges with respect to the titanium ion, approached those values obtained by Ye. A. Mel'nikova (the line of periods in Figure 2). With a humidity of 10 - 17 mm Hg, toxicity significantly dropped.

LD_{50} was, respectively, 0.1 and 0.4 mg/l (with respect to titanium). Symptoms of irritation of the ocular mucosa and the mucosa of the upper respiratory passages and severe difficulty in

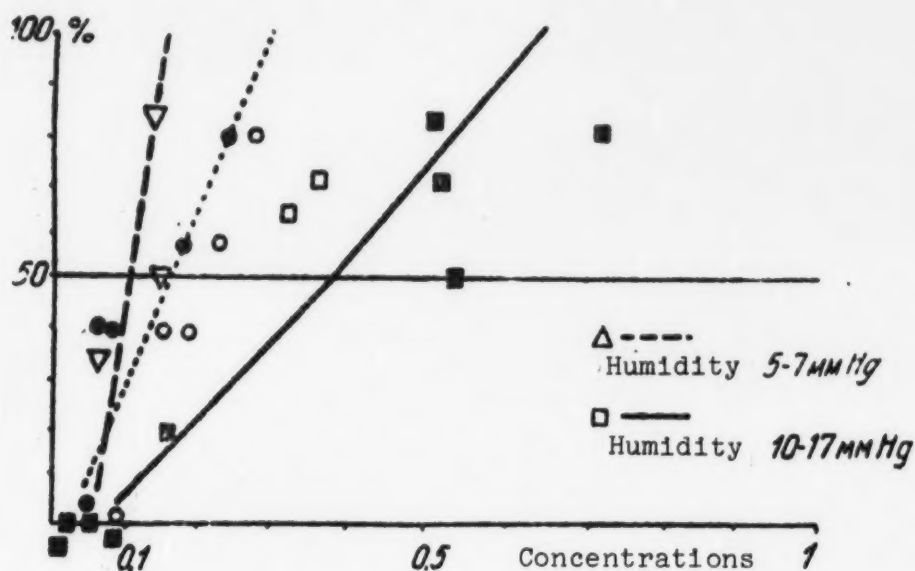


Figure 2. Mortality of albino mice during exposure to TiCl_4 , depending upon humidity. Each point was obtained on 10 animals. The line of periods represents the data of Ye. A. Mel'nikova

breathing were noted in the animals placed in the chamber soon after the beginning of supplying vapor of the products of hydrolysis of TiCl_4 . Movements were also difficult. Death ensued in this condition during dosing, or, as a rule, the first day afterward. Pre-mortem convulsions were observed. As a rule, if the animals survived the indicated term, they lived three weeks and one month after dosage. The surviving animals were less sensitive to the subsequent exposure to high concentrations of TiCl_4 lysis than the control animals (Figure 3).

Oxygen consumption decreased in the animals following single dosage, and there was an increase in the summative capacity of the central nervous system. The latter phenomenon can be explained by local irritation of the skin of the hind legs caused by the HCl liberated during hydrolysis. Edema and pulmonary hemorrhages were found at autopsy of the dead animals.

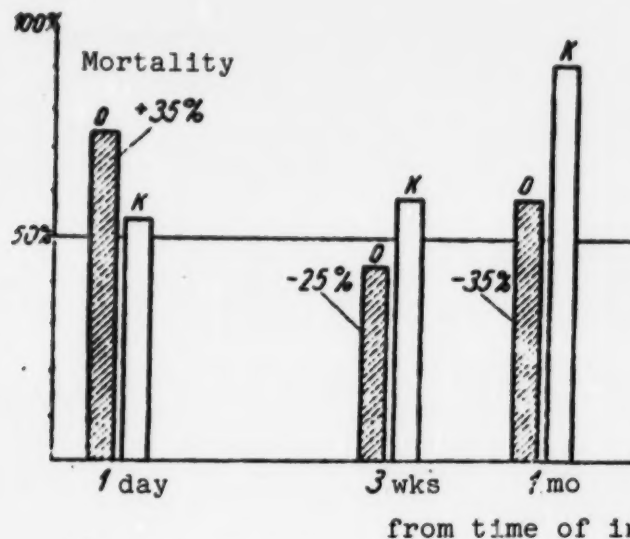


Figure 3. Change in sensitivity to $TiCl_4$ during repeated exposure

The reduction in $TiCl_4$ toxicity during increased humidity may be due to the increase in the rate of hydrolysis (and, consequently, by the entry into the organism of products containing fewer atoms of chlorine, and therefore capable of forming less HCl), and also to the change in dispersion of the formed aerosol.

With increased humidity, the expenditure of $TiCl_4$ required for creating the given concentration actually increased strongly; with a reduction in humidity, hydrolysis naturally decreased. In one case, vapor of undecomposed $TiCl_4$ was even found with a high atmospheric temperature (30°) (all chemical analyses were made by N. D. Babina).

During the analysis of dispersion of the aerosol taken in the dosage chamber with a relatively elevated humidity, it proved that the size of over 93% of the solid particles (products of decomposition of $TiCl_4$) and 63% of the drops was smaller than 2μ . At a lower humidity (5 - 7 mm Hg), the solid particles were significantly smaller. They were hardly detectable under the microscope or were of submicroscopic size. This may to a significant degree explain the increase in toxicity of the products of hydrolysis, since the

capacity of the particles to penetrate deeply into the lungs, as is known, is inversely proportional to their size.

The irritating effect of certain products of TiCl_4 decomposition was investigated on the tail skin of mice, on the back skin of the rabbit, and on the eye of the rabbit. Liquid TiCl_4 and the white solid product [assuming $\text{TiCl}(\text{OH})_3$], solution of this product in water 1 : 1 [assuming $\text{Ti}(\text{OH})_4$], were applied. The yellow solid product that vaporizes in air [with the assumption — $\text{TiCl}_2(\text{OH})_2$] was also applied.

Liquid TiCl_4 did not irritate the skin, but upon applying 1 drop to the eye for 10 seconds with subsequent copious washing with water, a suppurative conjunctivitis and darkening of the cornea developed. The solid white products did not irritate the skin but caused slight irritation of the conjunctiva. The solution of the indicated product in water caused a surface burn of the skin and hyperemia of the conjunctiva. The yellow substance displayed a stronger effect on the skin and the mucosa of the eyes than the white one.

Conclusions

1. With respect to the character of its effect, TiCl_4 is an irritant. The toxicity of TiCl_4 depended on atmospheric humidity. With an increase in humidity, the toxicity decreased. At an absolute humidity of 5 - 7 mm Hg, LD_{50} is approximately 0.1 mg/l, and at an absolute humidity of 10 - 17 mm Hg — 0.4 mg/l. A reduction in oxygen consumption, an increase in the summation capacity of the central nervous system, and death ensued with symptoms of edema and pulmonary hemorrhages in the poisoned animals. The animals that survived after a single inhalation dose were less sensitive to repeated exposure to this product a month after the first exposure.

2. At an absolute humidity of 10 - 17 mm Hg, the size of no less than 93% of the solid particles and 63% of the drops of TiCl_4 vapor-fog were less than 2 μ . Upon reducing humidity to 5 - 7 mm Hg, the size of the solid particles noticeably decreased.

3. Liquid TiCl_4 did not irritate the skin of the mouse tail, but upon application to the eye of the rabbit caused suppurative conjunctivitis and darkening of the cornea. Solid products of TiCl_4 lysis also irritated the eyes, but had practically no effect on the skin of the rabbit. Dissolving these substances in water (1 : 1) caused a surface burn effect.

4. The decrease in the toxicity of TiCl_4 with the increase in humidity requires further study, after which the indicated phenomenon may be used to improve conditions of industrial labor (washing surfaces with alkali water, etc.).